Ruthenium-Cobalt Alloy Electrodeposition

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Since little has been written about ruthenium alloy plating, the present work sets out to provide data on the electrodeposition of ruthenium-cobalt alloys, using a sulphate-sulphamate electrolyte. Some operating conditions have been obtained for the production of thin crack-free coatings of ruthenium-cobalt alloys.

There have been many developments in the electrodeposition of the platinum group metal alloys, platinum-cobalt and palladium-cobalt, which possess both perpendicular anisotropy and high coercive force, and are therefore being considered for a number of magneto-optic applications (1, 2). Recently a ternary alloy, platinum-ruthenium-cobalt, has been proposed for use as a magneto-optical recording medium (3). Ruthenium-cobalt alloys may also possess similar magnetic properties, but as yet there is no available data on this, and also there is no data in the literature on the electrodeposition of ruthenium-cobalt alloys. However, in the patent literature a process for alloying ruthenium with cobalt has been described, enabling ruthenium coatings containing several per cent of cobalt to be produced (4).

The present work therefore has been performed in order to obtain more information on the electrodeposition of ruthenium-cobalt alloys from a sulphate-sulphamate electrolyte, and to establish some conditions for the process.

Experimental Procedure

The electrolyte used for ruthenium plating was prepared from ruthenium(IV) hydroxychloride $Ru(OH)Cl_3$ and cobalt(II) sulphate-heptahydrate. The pH of the electrolyte was adjusted by adding either 20 per cent sodium hydroxide solution or dilute (1:1) sulphuric acid. The contents of the standard electrolyte used were, in mol/l: ~0.08 ruthenium(IV), ~1.5 cobalt(II), ~0.35 sulphuric acid and ~0.4 sulphamic acid. The pH was 1.7. The electrolytes from which ruthenium and cobalt were separately deposited contained similar amounts of all the components, except that cobalt(II) or ruthenium(IV) were excluded, respectively.

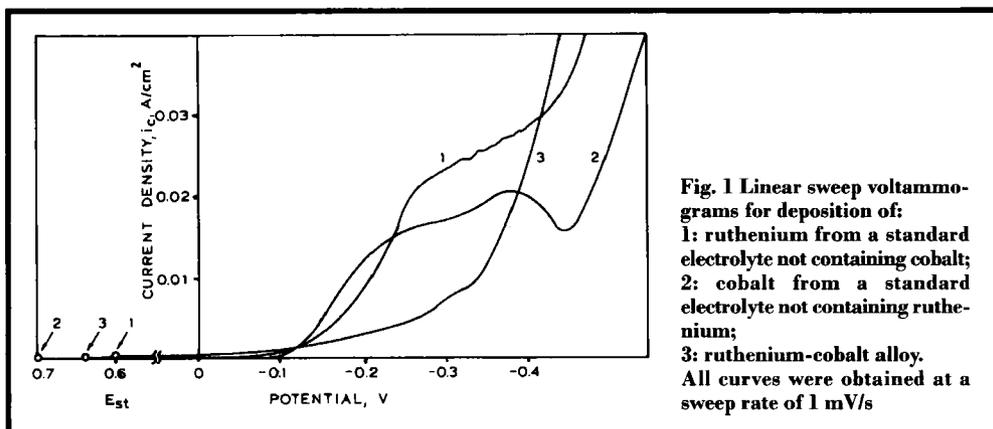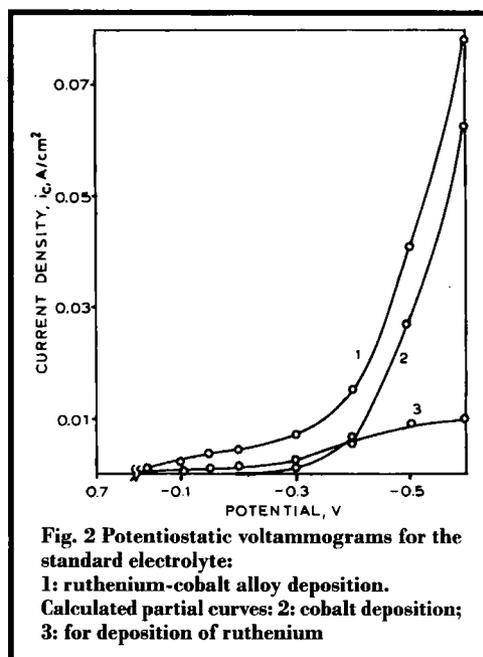Current density and potential measurements

Fig. 1 Linear sweep voltammograms for deposition of:
1: ruthenium from a standard electrolyte not containing cobalt;
2: cobalt from a standard electrolyte not containing ruthenium;
3: ruthenium-cobalt alloy.
All curves were obtained at a sweep rate of 1 mV/s

were carried out at a temperature of $60 \pm 0.5°C$ in air. The platinum electrode, of area 1 cm², was activated in 10 per cent sulphuric acid before each experiment and kept for 5 minutes in the electrolyte before the start of the experiment. The potentials are given versus a normal hydrogen electrode. A platinum plate of area 6 cm² served as the anode. Current efficiencies defined, according to Faraday's Law, as the weight of material deposited compared to that required theoretically, expressed as a percentage, were determined by the gravimetric method, taking into account alloy compositions which were determined by an X-ray electronic microanalyser. Partial curves were calculated from current efficiencies and alloy composition data, and were obtained under the potentiostatic conditions of the electrolysis.

Results and Discussions

The current density/potential studies show that there is no actual deposition of ruthenium or cobalt either separately or as an alloy within the potential range from the start-up potential, E_{st}, to 0 V, see Figure 1. When the pH of the electrolyte is 1.5 to 1.8, deposition of both metals begins at the same potential. When the pH is decreased the voltammograms for the separate depositions of ruthenium and cobalt shift to the region of less negative potential, the shift in the ruthenium voltammogram being the more significant. As can be seen in Figure 1, codeposition of both metals occurs with substantial polarisation at values of potential up to $- 0.35$ V, but with depolarisation at potentials more negative than $- 0.4$ V. The section of the ruthenium voltammograms at potentials ranging from $- 0.25$ V to $- 0.4$ V may be considered as corresponding to the limiting current, since a drop in the current efficiency for ruthenium electrodeposition was detected on increasing the current density, i_c, further. The same section of the cobalt curve cannot be taken to be the limiting current of cobalt, since the current efficiency increases with a further increase in current density. It has been found that the current efficiency of cobalt is 75 per cent at values for the current density of 0.01 A/cm² and is

Fig. 2 Potentiostatic voltammograms for the standard electrolyte:
1: ruthenium-cobalt alloy deposition.
Calculated partial curves: 2: cobalt deposition;
3: for deposition of ruthenium

95 per cent over the range of current density from 0.015 to 0.05 A/cm². This results in a considerable redistribution of the partial current densities of cobalt and ruthenium when increasing the current density, i_c, see Figure 2.

It should be noted that it is not possible to calculate the curve for hydrogen evolution from the data in Figure 2 due to the partial reduction of the ruthenium(IV) ions to lower oxidation states, namely ruthenium(III) and ruthenium(II), which occur on the cathode at the same time as the deposition of ruthenium and cobalt, and the evolution of hydrogen (5).

The results of these investigations show that it is possible to deposit ruthenium-cobalt alloy from a sulphate-sulphamate electrolyte. It can be seen from the data in Figure 3 that the composition of the alloy is greatly dependent on current density, i_c. This indicates that there is a possibility of obtaining modulated coatings of ruthenium-cobalt alloys by pulse-plating (6–8).

The dependence of the amount of cobalt in the ruthenium-cobalt alloy on the current density is not as great when the pH of the electrolyte is decreased to 1.0, see Figure 3. In Figure 4 the current efficiency of the alloy deposition is
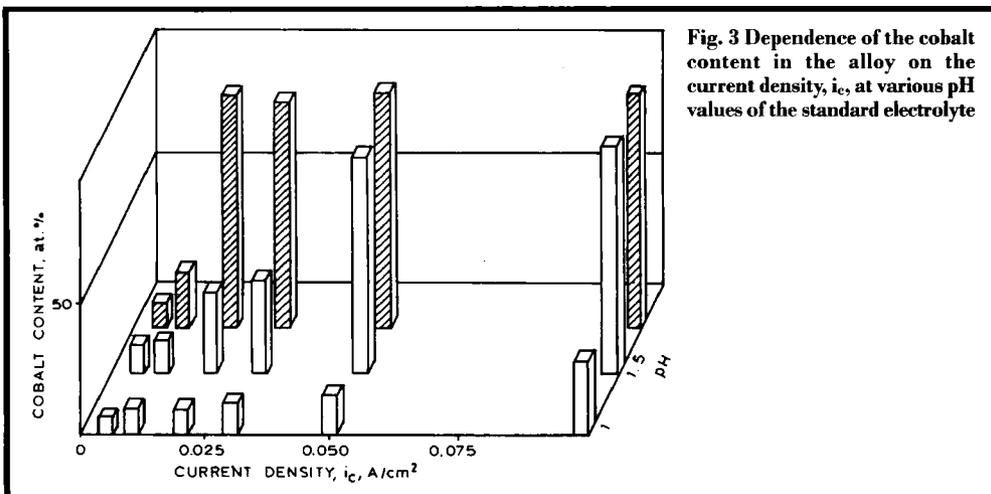
Fig. 3 Dependence of the cobalt content in the alloy on the current density, i_c, at various pH values of the standard electrolyte

shown to depend on the current density at different values of pH. By comparing Figures 3 and 4 it can be seen that the current efficiency is always higher when an alloy with high cobalt content is deposited. The current efficiency also decreases slightly with increasing temperature. This unexpected dependence is also apparent when the results shown in Figure 5 are examined; they show that the cobalt content in the alloy decreases when temperature is increased.

Experimental data therefore show that it is

possible to electrodeposit ruthenium-cobalt alloys containing different amounts of ruthenium and cobalt from a sulphate-sulphamate electrolyte. The composition of the alloy is determined by the pH of the electrolyte and by the value of the current density rather than by the ratio of metals in the electrolyte. The optimum composition of the electrolyte is, in mol/l: ~ 0.05 to 0.1 ruthenium(IV), ~ 1.0 to 1.5 cobalt(II), ~ 0.3 to 0.5 sulphuric acid, ~ 0.3 to 0.5 sulphamic acid and the pH of the electrolyte should be 1.2 to 2.0.

Semi-bright microcrystalline coatings, up to 2 μm thick, were obtained without cracks at deposition current densities ranging from 0.005 to 0.1 A/cm². In Figure 6 micrographs of the surface of ruthenium-cobalt alloy coatings are shown. It can be seen that the smoothest coatings are obtained at a current density of 0.01 A/cm², Figure 6(b). The size of crystallites is 0.03 μm. However, the coatings are not as smooth when they contain 85 per cent ruthenium and the current density is low. Coatings obtained at a current density of 0.015 A/cm², Figure 6(c), (and which contain only 10 to 15 per cent of ruthenium) typically have a similar surface structure. No sharp shaped crystallites or their aggregates were found; in fact, both the crystallites and the aggregates had a round (domed) shape.

Preliminary investigations of the magnetic properties of the ruthenium-cobalt coatings
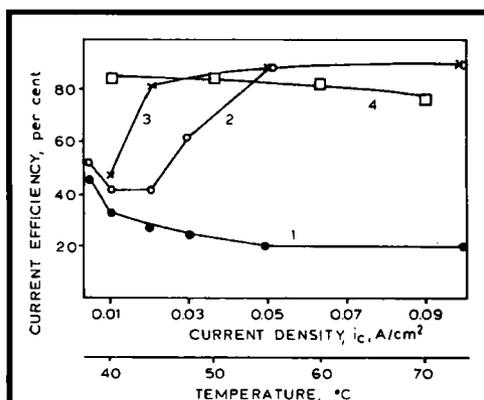

Fig. 4 Dependence of the current efficiency of the alloy deposition on: current density, i_c, in a standard electrolyte
1: at pH 1.0;   2: at pH 1.4;   3: at pH 1.7; and on: temperature, at i_c = 0.02 A/cm²
4: standard electrolyte at pH 1.7

show that the coercive force of films containing 40 to 60 atomic per cent of cobalt was about 300 Oe. The coercive force increased to 500 Oe when the films were deposited by pulse plating.

As has been noted earlier, ruthenium(IV) ions are partially reduced at the cathode. This produces some variations in the results when measuring current efficiency and alloy composition. To achieve maximum reproducibility the prepared electrolyte should be kept for not less than 3 days, then used at the operating current density for some hours, at about 2 Ah/l. Under these conditions the variation in the current efficiency and alloy compositions did not exceed 10 per cent. In order to prolong the life of the bath the electrodeposition should be carried out in an apparatus with separate anode and cathode compartments. The quality of the coatings in this case does not change after utilisation of 30 Ah/l of electrolyte. Depending upon the concentration of ruthenium(IV) ions, the electrolyte was adjusted by adding a ruthenium concentrate not containing sulphamic acid. A solution of sulphuric and sulphamic acids, both having a concentration of 0.4 mol/l, was used as the anolyte.

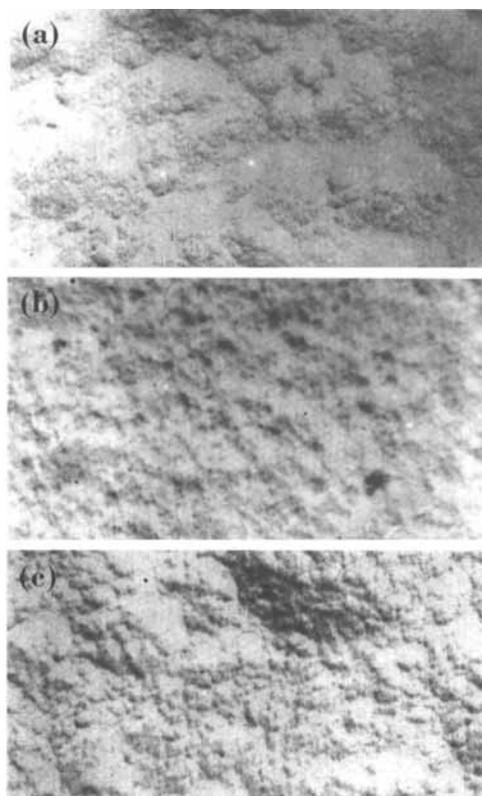In conclusion, ruthenium-cobalt alloys containing 10 to 85 per cent of cobalt were obtained

Fig. 6 Micrographs of the surface of ruthenium-cobalt alloy deposits obtained in standard electrolyte for current densities, in A/cm^2:(a) 0.005; (b) 0.01; (c) 0.015
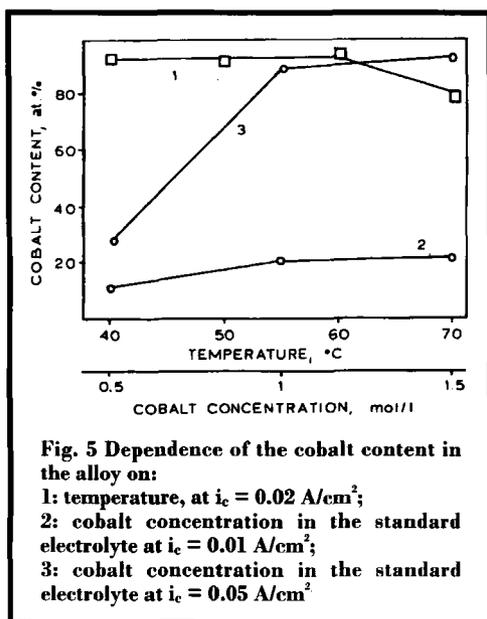

Fig. 5 Dependence of the cobalt content in the alloy on:
1: temperature, at i_c = 0.02 A/cm^2;
2: cobalt concentration in the standard electrolyte at i_c = 0.01 A/cm^2;
3: cobalt concentration in the standard electrolyte at i_c = 0.05 A/cm^2

from sulphate-sulphamate electrolyte. Crack-free semi-bright microcrystalline coatings, of thickness up to 2 μm, were obtained. The coercive force of the films reached up to 500 Oe. The electrolyte remained stable, even after utilisation at 30 Ah/l.

References

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